Conjugated Microporous Polymers Consisting of Tetrasubstituted [2.2]Paracyclophane Junctions

Yasuhiro Morisaki, Masayuki Gon, Yoshiki Chujo

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku,
Kyoto 615-8510, Japan
Correspondence to: Y. Morisaki (E-mail: ymo@chujo.synchem.kyoto-u.ac.jp) or Y. Chujo (E-mail: chujo@chujo.synchem.kyoto-u.ac.jp)

Received 18 December 2012; accepted 24 January 2013; published online
DOI: 10.1002/pola.26600

KEYWORDS: conjugated polymers; micropore; networks; [2.2]paracyclophane; polycondensation

INTRODUCTION [2.2]Paracyclophane, which contains two benzene rings,[1] has attracted considerable attention with regard to its structure, reactivity, and physical properties. A number of [2.2]paracyclophane derivatives have been prepared so far, and their unique properties derived from the characteristic interactions between the stacked π-electron systems have been investigated in detail.[1–3] Recently, we focused on [2.2]paracyclophane and synthesized through-space conjugated oligomers and polymers by incorporating [2.2]paracyclophane into the conjugated polymer backbone.[4–7] These polymers exhibited an extension of π-conjugation length via the through-space interaction.[8] In addition, end-capping of the through-space conjugated polymers allowed for fluorescence resonance energy transfer from the stacked π-electron systems to the end-capped π-electron systems.[8,9]

Microporous polymers such as metal organic frameworks,[10–20] porous coordination polymers,[10–20] and microporous organic polymers[21–33] have been extensively investigated. Because these polymers possess micropores and large surface areas, it is expected that they can be applied as catalysts,[34–38] gas storage materials,[26,31,33,39–43] and gas separation materials.[34,44,45] Generally, they are composed of organic compounds whose functional groups can be readily designed; thus, the sizes and shapes of the micropores can be controlled at the molecular level. Recently, π-conjugated frameworks have been used for network polymers. This new class of microporous network polymers is called conjugated microporous polymers (CMPs),[46,47] and they consist of only rigid π-conjugated skeletons and of micropores that can be readily fabricated. CMPs have received considerable attention owing to their potential application in the field of optoelectronics[48,49] because of the presence of delocalized π-electrons throughout their frameworks as well as their rigid micropores.

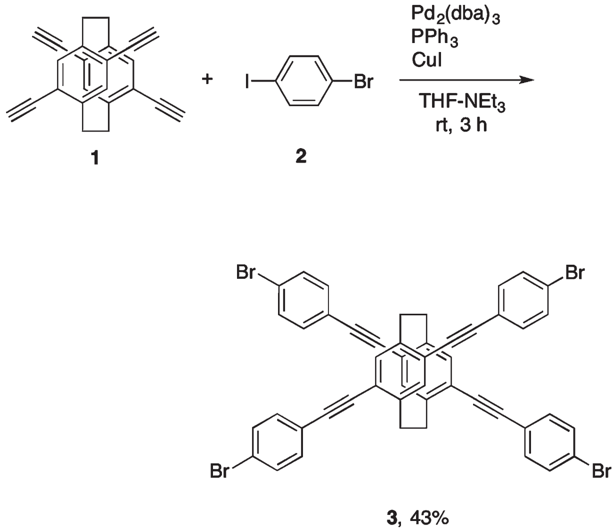
In this study, we focused on the structure of [2.2]paracyclophane to construct a network for a CMP. In particular, we selected a 4,7,12,15-tetrasubstituted [2.2]paracyclophane skeleton with a crisscross structure as the junction of the CMP. Three types of CMPs consisting of tetrasubstituted [2.2]paracyclophane junctions were synthesized from [2.2]paracyclophane monomers with different sizes by Hay coupling,[50] Sonogashira–Hagihara cross-coupling,[51,52] and Yamamoto coupling.[53] All CMPs were found to be microporous with large surface areas on the basis of nitrogen gas sorption studies. Further characterization of the obtained CMPs by cross-polarization magic angle spinning (CP/MAS) ^{13}C NMR, FTIR, X-ray diffraction (XRD), and scanning electron microscopy (SEM) were also performed.

EXPERIMENTAL

General

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX400 instrument at 400 and 100 MHz, respectively. Samples were analyzed in $CDCl_3$, and the chemical shift values were expressed relative to Me_4Si as an internal standard. Solid state cross-polarization/magic-angle-sample-spinning (CP/MAS) ^{13}C NMR spectra were obtained on a Bruker Avance III spectrometer operated at 100 MHz, and CP/MAS spectra were recorded at the MAS rate of 7 kHz with the ^{1}H decoupling field amplitude of 57 kHz. The contact time and the repetition time were fixed as 2 ms and 5 s, respectively. Analytical thin layer chromatography was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel C-300 SiO_2. High-resolution mass spectra (HRMS) were obtained on a Thermo Scientific MALDI LTQ Orbitrap XL hybrid mass spectrometer. The adsorption isotherms of nitrogen at 77 K were measured with a BELSORP-18PLUS instrument, and N_2 gas of high purity (99.9999%) was used. Prior to the adsorption

Additional Supporting Information may be found in the online version of this article.

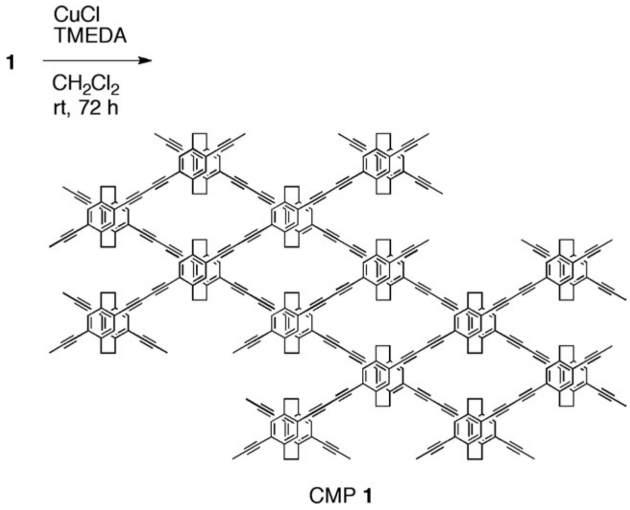


SCHEME 1 Synthesis of monomer **3**.

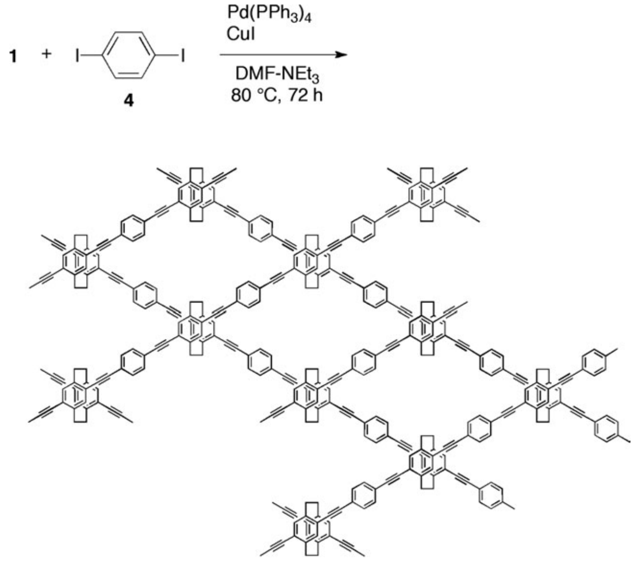
measurements, the sample was treated under reduced pressure ($<10^{-2}$ Pa) at 423 K for 5 h. SEM measurement was carried out on a JEOL JSM-5600B system. Samples were put on a conducting carbon tape attached by a SEM grid, and then coated with platinum. XRD data were obtained on a Rigaku MiniFlex diffractometer using CuKα radiation in a range of $3° \leq 2\theta \leq 60°$ at intervals of 0.01° at a scanning rate of 0.25° min^{-1}. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials

THF and Et$_3$N were purchased and purified by passage through purification column under Ar pressure.[54] Dehydrated CH$_2$Cl$_2$ and DMF were obtained commercially, and used after degassing. Pd$_2$(dba)$_3$, Pd(PPh$_3$)$_4$, Ni(cod)$_2$, PPh$_3$, CuI, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), 2,2′-bipyridine, 1-bromo-4-iodobenzene (**2**), and 1,4-diiodobenzene (**4**) were obtained commercially, and used without further purification. Cyclooctadiene (COD) was obtained commercially, and used after purification by distillation. 4,7,12,15-Tetraethynyl[2.2]paracyclophane (**1**)[55] was prepared from the corresponding tetrabromo[2.2]paracyclophane[56] as described in the literature.



SCHEME 2 Synthesis of CMP **1** by Hay coupling.



SCHEME 3 Synthesis of CMP **2** by Sonogashira–Hagihara cross-coupling.

Monomer Synthesis

Compound 3

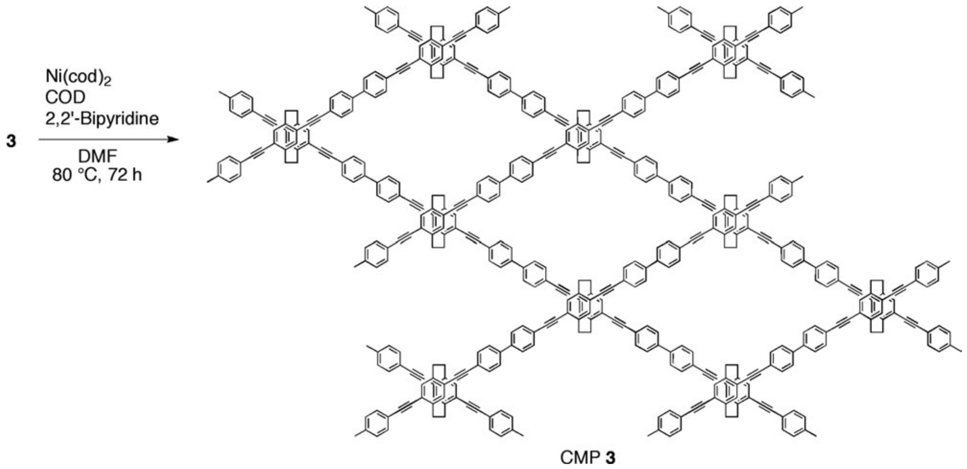
The mixture of **1** (0.363 g, 1.19 mmol), **2** (1.486 g, 5.25 mmol), Pd$_2$(dba)$_3$ (109 mg, 0.12 mmol), PPh$_3$ (125 mg, 0.45 mmol), and CuI (46 mg, 0.24 mmol) were placed in a 50 mL Pyrex flask equipped with a magnetic stirrer bar. The equipment was purged with Ar, followed by adding THF (40 mL) and NEt$_3$ (10 mL) at 0 °C. The reaction was carried out at room temperature for 3 h. The reaction mixture was concentrated *in vacuo* to afford the crude product, which was purified by SiO$_2$ column chromatography (hexane/CHCl$_3$, v/v = 8/1 as an eluent) and recrystallization from CHCl$_3$ and MeOH to afford **3** as a pale yellow solid (476 mg, 0.52 mmol, 43%). $R_f = 0.24$ (hexane/CHCl$_3$, v/v = 8/1).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.07 (t, J = 8.0 Hz, 4H), 3.54 (t, J = 8.0 Hz, 4H), 7.10 (s, 4H), 7.41 (d, J = 8.0 Hz, 8H), 7.53 (d, J = 8.0 Hz, 8H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 32.7, 90.3, 93.6, 122.3, 122.7, 125.0, 131.7, 132.8, 134.6, 141.8. HRMS (MALDI) calcd for $C_{48}H_{28}Br_4$, 919.8919; found 919.8878 [M]$^+$. Anal. calcd for $C_{48}H_{28}Br_4$: C 62.37 H 3.05 Br 34.58, found: C 62.64 H 3.27 Br 34.48.

Polymer Synthesis

CMP 1

CuCl$_2$ (99 mg, 1.00 mmol), TMEDA (116 mg, 1.00 mmol), and CH$_2$Cl$_2$ (5.0 mL) were placed in a 50 mL Pyrex flask equipped with a magnetic stirrer bar, and the mixture was bubbled with O$_2$ for 30 min. To this solution compound **1** (126 mg, 0.42 mmol) in CH$_2$Cl$_2$ (2.0 mL) was added. After the reaction was carried out at room temperature for 72 h,



SCHEME 4 Synthesis of CMP **3** by Yamamoto coupling.

aqueous NH_3 (28%) was added. The pale yellow solid was collected by filtration and washed with THF, hexane, $CHCl_3$, H_2O, and MeOH. Then, the solid was further washed with $CHCl_3$ for 24 h and MeOH for 24 h using a Soxhlet extractor. The solid was dried at 150 °C in a vacuum oven for 24 h to afford CMP **1** (112 mg, 90%). Solid state CP/MAS ^{13}C NMR: 31.7, 82.7, 125.2, and 141.1 ppm. FTIR (KBr): 903, 1470, 1573, 2158, 2929, and 3290 cm^{-1}.

CMP 2

A mixture of **1** (72 mg, 0.24 mmol), **8** (157 mg, 0.48 mmol), $Pd(PPh_3)_4$ (27.4 mg, 0.024 mmol), CuI (4.5 mg, 0.024 mmol), Et_3N (1.9 mL), and DMF (2.85 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar and a reflux condenser. After degassing the reaction mixture several times, the reaction was carried out at 80 °C for 72 h with stirring. The reaction mixture was cooled to room temperature, and 1.0 N HCl (10 mL) was added to the mixture. The pale yellow solid was collected by filtration and washed with THF, hexane, $CHCl_3$, H_2O, and MeOH. Then, the solid was further washed with $CHCl_3$ for 24 h and MeOH for 24 h using a Soxhlet extractor. The solid was dried at 150 °C in a vacuum oven for 24 h to afford CMP **2** (124 mg, 116%). Solid state CP/MAS ^{13}C NMR: 31.7, 94.6, 123.4, 130.1, 140.2 ppm. FTIR (KBr): 833, 905, 1508, 1593, 2195, 2930, 3032, and 3296 cm^{-1}.

CMP 3

A mixture of $Ni(cod)_2$ (309 mg, 1.12 mmol), and 2,2′-bipyridine (175.7 mg, 1.12 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar and a reflux condenser. The equipment was purged with Ar, followed by adding DMF (30 mL) and COD (0.14 mL, 1.12 mmol), and then, the mixture was stirred for 1 h at 80 °C. To the mixture was added compound **3** (200 mg, 0.22 mmol). The reaction was carried out at 80 °C for 72 h. To the mixture, conc HCl aq (6.0 mL) was added, and the mixture was stirred for 8 h at room temperature. The pale yellow solid was collected by filtration and washed with THF, hexane, $CHCl_3$, H_2O, and MeOH. Then, the solid was further washed with $CHCl_3$ for 24 h and MeOH for 24 h using a Soxhlet extractor. The solid was dried at 150 °C in a vacuum oven for 24 h to afford CMP **3** (120 mg, 91%). Solid state CP/MAS ^{13}C NMR: 31.6, 96.5, 126.1, 130.5, 140.1 ppm. FTIR (KBr): 822, 1497, 1601, 2181, 2930, 3028 cm^{-1}.

^{1}H and ^{13}C NMR spectra of **3**, and solid state CP/MAS ^{13}C NMR spectra and FTIR spectra of CMPs **1**–**3** are shown in Supporting Information.

TABLE 1 Results of Polymerization and Surface Areas of CMPs

			Elemental analysis				
CMP	Yield[a] (%)	Reaction Efficiency[b]	H (%) Found, Calcd	C (%) Found, Calcd	Halogen (%) Found, Calcd	S_{BET} (m^2 g^{-1})	$S_{Langmuir}$ (m^2 g^{-1})
1	90	0.72	4.05, 4.03	90.55, 95.97	–	889	1,156
2	116	0.94	4.72, 4.46	85.32, 95.54	Iodine: 3.37, 0	840	1,285
3	91	>0.99	4.98, 4.67	87.93, 95.33	Bromine: 0.24, 0	956	1,231

[a] Isolated yield calculated on the basis of weight.

[b] Calculated from the elemental analysis data for CMPs **2** and **3**, and from the FTIR absorption peak of the terminal alkyne C—H stretching for CMP **1**.

RESULTS AND DISCUSSION

[2.2]Paracyclophane-based monomer **1** was prepared from 4,7,12,15-tetrabromo[2.2]paracyclophane[56] using the procedure reported in the literature.[55] The Sonogashira–Hagihara cross-coupling[51,52] of compound **1** with 1-bromo-4-iodobenzene (**2**) proceeded chemoselectively to give monomer **3** in 43% isolated yield, as shown in Scheme 1. Schemes 2–4 show the syntheses of target CMPs **1**–**3**. Hay coupling[50] of **1** (Scheme 2), Sonogashira-Hagihara cross-coupling of **1** with **4** (Scheme 3), and Yamamoto coupling[53] of **3** (Scheme 4) afforded the corresponding CMPs **1**–**3**, respectively. After the coupling reaction, the crude products were washed with organic solvents and H_2O using a Soxhlet extractor to yield the CMPs as pale yellow powders. The polymerization results are listed in Table 1. The reaction efficiencies of the CMPs were calculated according to the FTIR absorption peak of the C—H stretching vibration of the terminal alkyne (CMP **1**) and the elemental analysis data (CMPs **2** and **3**). Generally, the isolated yield of a CMP synthesized by palladium-catalyzed cross-coupling is greater than 100% because of the presence of unreacted halogens such as bromine and iodine. Thus, in our case, CMP **2** possessed 3.37% iodine according to the result of elemental analysis. On the other hand, Yamamoto coupling proceeded smoothly to provide CMP **3** (Scheme 4) with high reaction efficiency (>0.99), although this reaction required a stoichiometric amount of the Ni complex. Almost all of the Br species reacted, and the elemental analysis showed that only 0.24 wt % of Br remained in the sample. It is desirable to remove residual halogens from the viewpoint of the possible application of the CMPs to optical materials.

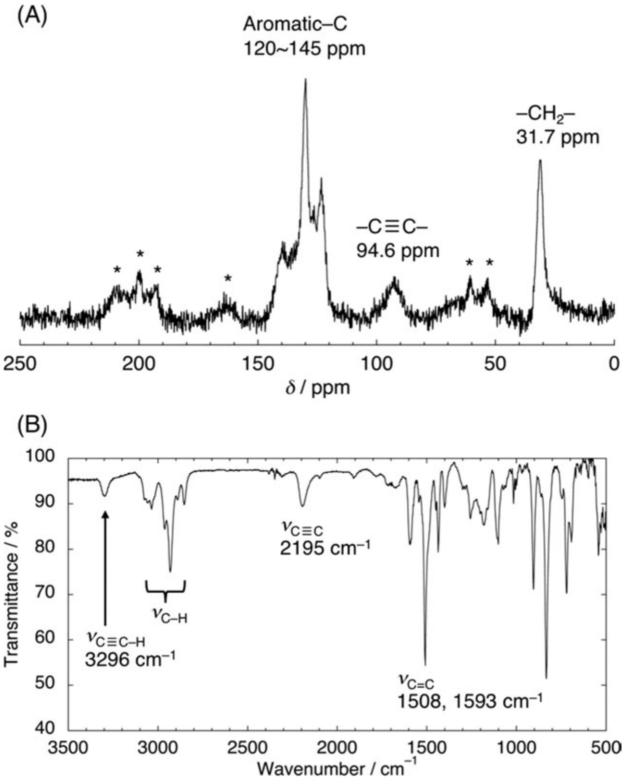


FIGURE 1 (A) Solid state CP/MAS ^{13}C NMR spectrum of CMP **2**; CP/MAS 7 kHz, asterisk denotes spinning sidebands. (B) FTIR spectrum of CMP **2** (KBr).

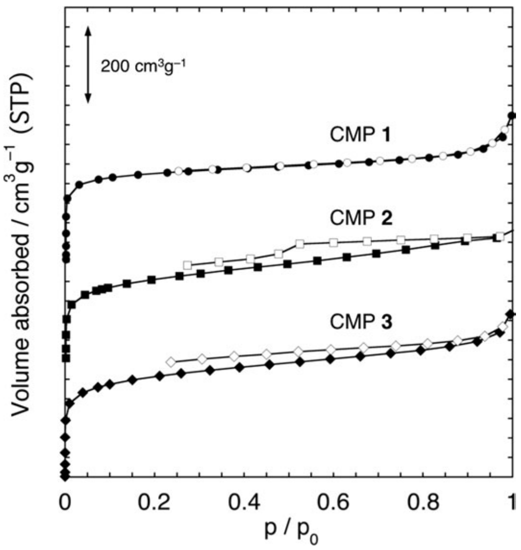


FIGURE 2 Nitrogen adsorption–desorption isotherms of CMPs **1**–**3** at 77 K; a filled symbol and an open symbol indicate adsorption and desorption isotherms, respectively.

The structures of the obtained CMPs were confirmed by solid-state CP/MAS ^{13}C NMR and FTIR spectroscopies. As a representative example, the solid-state CP/MAS ^{13}C NMR spectrum of CMP **2** is shown in Figure 1(A). The signal positions for various types of carbons were as follows. The relatively sharp peak at 31.7 ppm was assigned to the bridge methylene carbons of cyclophane units. The small signals of the C—C triple bond carbons appeared at around 95 ppm. Finally, the peaks at 120–145 ppm were assignable to the aromatic carbons. The FTIR spectra were obtained using KBr pellets of the CMPs. The spectrum of CMP **2** is shown in Figure 1(B), and the spectra of CMPs **1** and **3** are shown in Supporting Information. For all samples, the peaks of the stretching vibration of the C—C triple bond appeared around 2200 cm^{-1} and that of the C—C double bonds of phenylenes appeared around 1580 and 1480 cm^{-1}. The peaks attributable to the stretching vibrations of the C—H bonds in the cyclophane units were observed at 2850–2950 cm^{-1}. In the FTIR spectra of CMPs **1** (Fig. S4 in Supporting Information) and **2** [Fig. 1(B)], the C—H stretching vibration of unreacted terminal alkynes appeared at around 3250 cm^{-1}. Thus, the reaction efficiencies of CMPs **1** and **2** could be calculated from the absorbance of the terminal alkyne C—H stretching.

The CMPs were analyzed by nitrogen gas sorption. The nitrogen adsorption/desorption isotherms of CMPs **1**–**3** obtained at 77 K are shown in Figure 2. According to the IUPAC classification reported in 1985,[57] all isotherms of CMPs **1**–**3** exhibited a type I nitrogen gas sorption profile. This result clearly indicates that the obtained CMPs are microporous network polymers comprised only micropores with diameters of less than 2 nm. The Brunauer–Emmett–Teller (BET) surface areas (S_{BET}) and Langmuir surface areas (S_{Langmuir}) of CMPs **1**–**3** were estimated, and the results are shown in Table 1. All of the CMPs exhibited large BET surface areas greater than 840 m^2 g^{-1}. CMP **3**, which was obtained by Yamamoto coupling, exhibited the highest S_{BET} value of approximately 1000 m^2g^{-1}. Pore size distribution curves of CMPs **1**–**3** were obtained by the micropore method, and they are shown in Figure S9 in Supporting Information. The pores were mainly observed in the mesopores range from 0.5 to 1.1 nm. The pore diameters of the CMPs increased as the distance between [2.2]paracyclophane junctions became longer. For example, the pore diameters of CMPs **2** and **3** were estimated to be approximately 1.0 nm.

The powder XRD patterns of CMPs **1**–**3** exhibited the hollow peaks as shown in Figure S10 in Supporting Information, indicating that they were completely amorphous. SEM images of CMPs **1**–**3** providing morphological information are shown in Supporting Information Figures S11(A–C), respectively. The morphology of CMP **2** obtained by cross-coupling polymerization suggested the presence of various chunks consisting of small plates and blocks [Fig. S11(B)]. In contrast, the SEM image of CMP **1** showed aggregates consisting of small blocks [Fig. S11(A)], and that of CMP **3**, which was prepared by the Yamamoto coupling, showed relatively uniform particles with approximately 0.2 μm in size [Supporting Information Fig. S11(C)]. Thus, CMP **3** was readily dispersed in common organic solvents such as $CHCl_3$ and CH_2Cl_2. In addition, there was little residual Br in CMP **3**; therefore, its optical properties were investigated. As shown in Supporting Information Figure S12(A), CMP **3** dispersed in CH_2Cl_2 exhibited a broad absorption band with a peak top at around 420 nm. As shown in Supporting Information Figure S12(B), upon excitation at the absorption peak maximum, a broad and featureless emission spectrum was observed with a peak top at around 530 nm (fluorescence quantum yield of 2%) derived from the stacked and aggregated structures of the π-conjugated frameworks. Encapsulation of guest molecules into this class of CMPs and their application as a light-harvesting antenna are the next target.

In summary, we have prepared CMPs containing tetrasubstituted [2.2]paracyclophane units as the junctions of the network structure by Hay coupling, Sonogashira–Hagihara cross-coupling, and Yamamoto coupling. All CMPs comprised micropores with diameters of less than 2 nm. Moreover, they exhibited large surface areas; in particular, the BET surface area (S_{BET} value) of the CMP synthesized by Yamamoto coupling reached 1000 m^2 g^{-1}. The morphology of this CMP was relatively uniform and the particles had diameters of approximately 0.2 μm; therefore, it was readily dispersed in common organic solvents. The polymer networks can be tuned by introducing various aromatic units into the cyclophane monomer. Further studies will concentrate on the application of the CMPs consisting of tetrasubstituted [2.2]paracyclophane junctions as host materials for light-harvesting antennae and metal-supported catalysts.

ACKNOWLEDGMENTS

Financial support “Grant-in-Aid for Young Scientists (A) (No. 21685012)” from the Ministry of Education, Culture, Sports, Science and Technology, Japan is gratefully acknowledged. This work was partially supported by The Asahi Glass Foundation and “Grant-in-Aid for Young Scientists (A) (No. 24685018)” from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors are grateful to Professor Susumu Kitagawa and Dr Munehiro Inukai (Department of Synthetic Chemistry and Biological Chemistry, Kyoto University) for solid state CP/MAS ^{13}C NMR spectroscopy and valuable discussions.

REFERENCES AND NOTES

1 C. J. Brown, A. C. Farthing, *Nature* **1949,** *164*, 915–916.

2 Cyclophane Chemistry: Synthesis, Structures and Reactions; F. Vögtle, Ed.; Wiley: Chichester, **1993.**

3 Modern Cyclophane Chemistry; R. Gleiter, H. Hopf, Eds.; Wiley-VCH: Weinheim, Germany, **2004.**

4 Y. Morisaki, Y. Chujo, *Angew. Chem. Int. Ed. Engl.* **2006,** *45*, 6430–6437.

5 Y. Morisaki, Y. Chujo, *Prog. Polym. Sci.* **2008,** *33*, 346–364.

6 Y. Morisaki, Chujo Y. *Polym. Chem.* **2011,** *2*, 1249–1257.

7 Y. Morisaki, Y. Chujo, In Conjugated Polymer Synthesis: Methods and Reactions; Y. Chujo, Ed.; Wiley-VCH: Weinheim; **2010;** Chapter 5, pp 133–163.

8 Y. Morisaki, S. Ueno, A. Saeki, A. Asano, S. Seki, Chujo Y. *Chem. Eur. J.* **2012,** *18*, 4216–4224.

9 Y. Morisaki, S. Ueno, Chujo Y. *J. Polym. Sci. Part A: Polym. Chem.* **2013,** *51*, 334–339.

10 H. Li, M. Eddaoudi, M. O’Keeffe, O. M. Yaghi, *Nature* **1999,** *402*, 276–279.

11 A. K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem. Int. Ed. Engl.* **1999,** *38*, 3268–3292.

12 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, M. O’Keeffe, O. M. Yaghi, *Science* **2002,** *295*, 469–472.

13 O. M. Yaghi, M. O’Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003,** *423*, 705–714.

14 A. Matzger, M. O’Keeffe, O. M. Yaghi, *Nature* **2004,** *427*, 523–527.

15 S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem., Int. Ed. Engl.* **2004,** *43*, 2334–2375.

16 S. Kitagawa, S. Noro, T. Nakamura, *Chem. Commun.* **2006,** 701–707.

17 S. Kitagawa, R. Matsuda, *Coord. Chem. Rev.* **2007,** *251*, 2490–2509.

18 T. K. Maji, S. Kitagawa, *Pure Appl. Chem.* **2007,** *79*, 2155–2177.

19 G. Férey, *Chem. Soc. Rev.* **2008,** *37*, 191–214.

20 T. Uemura, N. Yanai, S. Kitagawa, *Chem. Soc. Rev.* **2009,** *38*, 1228–1236.

21 J.-X. Jiang, A. I. Cooper, *Top. Curr. Chem.* **2010,** *293*, 1–33.

22 A. Thomas, *Angew. Chem., Int. Ed. Engl.* **2010,** *49*, 8328–8344.

23 A. Thomas, P. Kuhn, J. Weber, M.-M. Titirici, M. Antonietti, *Macromol. Rapid Commun.* **2009,** *30*, 221–236.

24 N. B. McKeown, P. M. Budd, *Chem. Soc. Rev.* **2006,** *35*, 675–683.

25 P. M. Budd, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib, C. E. Tattershall, *Chem. Commun.* **2004,** 230–231.

26 N. B. McKeown, B. M. Gahnem, K. Msayib, P. M. Budd, C. E. Tattershall, K. Mahmood, S. Tan, D. Book, H. W. Langmi, A. Walton, *Angew. Chem., Int. Ed. Engl.* **2006,** *45*, 1804–1807.

27 P. M. Budd, A. Butler, J. Selbie, K. Mahmood, N. B. McKeown, B. Ghanem, K. Msayib, D. Book, A. Walton, *Phys. Chem. Chem. Phys.* **2007,** *9*, 1802–1808.

28 B. S. Ghanem, K. J. Msayib, N. B. McKeown, K. D. M. Harris, Z. Pan, P. M. Budd, A. Butler, J. Selbie, D. Book, A. Walton, *Chem. Commun.* **2007,** 67–69.

29 A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger, O. M. Yaghi, *Science* **2005,** *310*, 1166–1170.

30 H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, R. E. Taylor, M. O'Keeffe, O. M. Yaghi, *Science* **2007,** *316*, 268–272.

31 J. Y. Lee, C. D. Wood, D. Bradshaw, M. J. Rosseinsky, A. I. Cooper, *Chem. Commun.* **2006,** 2670–2672.

32 M. P. Tsyurupa, V. A. Davankov, *React. Funct. Polym.* **2006,** *66*, 768–779.

33 C. D. Wood, B. Tan, A. Trewin, H. J. Niu, D. Bradshaw, M. J. Rosseinsky, Y. Z. Khimyak, N. L. Campbell, R. Kirk, E. Stockel, A. I. Cooper, *Chem. Mater.* **2007,** *19*, 2034–2048.

34 N. B. McKeown, P. M. Budd, K. J. Msayib, B. S. Ghanem, H. J. Kingston, C. E. Tattershall, S. Makhseed, K. J. Reynolds, D. Fritsch, *Chem. Eur. J.* **2005,** *11*, 2610–2620.

35 A. Taguchi, F. Schüth, *Micropor. Mesopor. Mater.* **2005,** *77*, 1–45.

36 M. Hartmann, *Chem. Mater.* **2005,** *17*, 4577–4593.

37 A. Corma, H. Garcia, *Adv. Synth. Catal.* **2006,** *348*, 1391–1412.

38 X. Du, Y. L. Sun, B. E. Tan, Q. F. Teng, X. J. Yao, C. Y. Su, W. Wang, *Chem. Commun.* **2010,** *46*, 970–972.

39 C. D. Wood, B. Tan, A. Trewin, F. Su, M. J. Rosseinsky, D. Bradshaw, Y. Sun, L. Zhou, A. I. Cooper, *Adv. Mater.* **2008,** *20*, 1916–1921.

40 H. Furukawa, O. M. Yaghi, *J. Am. Chem. Soc.* **2009,** *131*, 8875–8883.

41 A. U. Czaja, N. Trukhan, Müller, U. *Chem. Soc. Rev.* **2009,** *38*, 1284–1293.

42 F. Svec, J. Germain, J. M. J. Fréchet, *Small* **2009,** *5*, 1098–1111.

43 A. Li, R. F. Lu, Y. Wang, X. Wang, K. L. Han, W. Q. Deng, *Angew. Chem., Int. Ed. Engl.* **2010,** *49*, 3330–3333.

44 H. B. Park, C. H. Jung, Y. M. Lee, A. J. Hill, S. J. Pas, S. T. Mudie, E. Van Wagner, B. D. Freeman, D. J. Cookson, *Science* **2007,** *318*, 254–258.

45 H. Ren, T. Ben, E. S. Wang, X. F. Jing, M. Xue, B. B. Liu, Y. Cui, S. L. Qiu, G. S. Zhu, *Chem. Commun.* **2010,** *46*, 291–293.

46 A. I. Cooper, *Adv. Mater.* **2009,** *21*, 1291–1295.

47 N. B. McKeown, P. M. Budd, *Macromolecules* **2010,** *43*, 5163–5176.

48 L. Chen, Y. Honsho, S. Seki, D.-L. Jiang, *J. Am. Chem. Soc.* **2010,** *132*, 6742–6748.

49 X. Liu, Y. Xu, D.-L. Jiang, *J. Am. Chem. Soc.* **2012,** *134*, 8738–8741.

50 A. S. Hay, *J. Org. Chem.* **1962,** *27*, 3320–3321.

51 Y. Tohda, K. Sonogashira, N. Hagihara, *Synthesis* **1977,** 777–778.

52 Sonogashira K. In Handbook of Organopalladium Chemistry for Organic Synthesis; E. Negishi, Ed.; Wiley-VCH: New York, **2002, pp.** 493–529.

53 T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z.-H. Zhou, Y. Nakamura, T. Kanbara, *Macromolecules* **1992,** *25*, 1214–1223.

54 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996,** *15*, 1518–1520.

55 L. Bondarenko, I. Dix, H. Hinrichs, H. Hopf, *Synthesis* **2004,** 2751–2759.

56 H.-F. Chow, K.-H. Low, K. Y. Wong, *Synlett* **2005,** 2130–2134.

57 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol, T. Siemieniewska, *Pure Appl. Chem.* **1985,** *57*, 603–619.